

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

VOL. 8

MAY, 1923

No. 5

THE ISOMORPHISM OF ALBITE AND ANORTHITE¹

FERRUCCIO ZAMBONINI, *University of Naples*

ABSTRACT BY H. S. WASHINGTON, *Geophysical Laboratory,
Carnegie Institution of Washington*

INTRODUCTION

In the January (1923) number of THE AMERICAN MINERALOGIST Dr. E. T. Wherry has expounded his interesting and suggestive views on "Volume Isomorphism in Silicates," the fundamental idea being that atoms that have approximately equal volumes can replace each other "isomorphously," while those with widely different volumes cannot. Wherry minimizes the importance of valency in such isomorphous replacement and disbelieves in the necessity of equality in the sums of the valencies of the replacing atoms.

During the discussion of Wherry's paper I not only "called attention to the fact that Professor Zambonini is working along similar lines," as Dr. Wherry says in a foot-note, but stated that Zambonini's views regarding the relations of atomic diameters or volumes² to isomorphism are essentially identical with those of Wherry. I also commented on the interest that lay in the fact that two workers had independently and almost simultaneously arrived at almost identical conclusions, and remarked that this independent agreement was a strong point in favor of the probable correctness of the new explanation of certain cases of isomorphism.

Before beginning the abstract of Professor Zambonini's paper, I trust that I may be permitted a word of introductory personal explanation. In May, 1922, on the train between Naples and Rome, Professor Zambonini explained to me his theory at some length, and asked me to publish an abstract of his forthcoming paper in an American scientific journal, to which request I assented. He sent me later a separate of his paper whose title is

¹ F. Zambonini, *Rend. Accad. Lincei*, **31**, 295-301, (April 23), 1922.

² Zambonini speaks in terms of atomic diameters, while Wherry uses atomic volumes; the fundamental ideas are the same.

given above, but unfortunately, the publication of the abstract was delayed. The publication of this abstract at the present time seems to be especially desirable, not only in justice to Professor Zambonini, and in fulfillment of my promise to him, but so that American mineralogists may be able to compare the views of Zambonini and Wherry, as the Italian journal is accessible with difficulty in this country. In the following abstract most of the paper will be summarized very briefly, but the more important passages will be given in full in literal translation.

THE ABSTRACT

In the first three pages Professor Zambonini discusses the isomorphism of albite and anorthite and the various explanations that have been advanced for the demonstrated isomorphism in spite of the difference in type of chemical formula of the two minerals. He calls attention to the observation of Hiortdahl³ that in certain cases of such isomorphism there is equality of the total valencies of the replacing elements, and he accepts the suggestion of Groth⁴ that in the change from albite to anorthite there is substitution of a group CaAl for the group NaSi , with equal sums of the principal valencies.

"We are dealing, certainly, with facts that do not enter into the ordinary isomorphous substitutions of "vicariant" elements, because in such cases an atom of calcium should replace two atoms of sodium, as is seen in so many minerals. Is it possible to give a plausible explanation of these singular substitutions, atom for atom, of elements of different valencies? I think that one can do so, if one takes into account the recent very important researches of W. L. Bragg⁵ on the arrangement of the atoms in crystals, from which he has been able to calculate the atomic diameter of the various elements.

"According to Bragg the atomic diameter of silicon is 2.35 \AA and that of aluminum is 2.70 \AA , the difference, as can be seen from Bragg's table, being of the same order of magnitude as differences between some atoms which are certainly "vicariant." One can thus understand how an atom of aluminum can take the place of one of silicon in the crystal structure of albite without bringing about notable change [in form].

³ T. Hiortdahl, *Zeits. Kryst.*, **12**, 416, 1887.

⁴ P. Groth, *Chemische Krystallographie*, **2**, 275, 1908. For an extended application of Groth's suggestion see H. S. Washington, *Am. J. Sci.*, **34**, 555, 1912.

⁵ W. L. Bragg, *Phil. Mag.*, **40**, 169, 1920.

"The conditions in the case of sodium and calcium are still more favorable, because the atomic diameters of these two elements are respectively 3.55 and 3.40 Å. The fact is also noteworthy that the smaller atomic diameter of calcium relative to that of sodium largely compensates for the difference between the atomic diameters of aluminum and silicon. In its entirety, the change from albite to anorthite takes place with a difference in the sum of the atomic diameters of only 0.2 Å, which is practically negligible if one considers that one is dealing with a complex of some thirteen atoms.

"An atom of aluminum can take the place of one of silicon, not only because of the small difference between the atomic diameters of the two elements, but also because aluminum presents some interesting relations with silicon. Aluminum is, in fact, a notably amphoteric element and it can thus assume the acid function which is played by silicon; besides which, and this is very important, aluminum is one of the two heterologues of silicon itself. To this combination of circumstances is due the power that aluminum has of replacing silicon, atom by atom, in certain silicates.

"The fact that the replacement, in the crystal edifice of albite, of an atom of silicon by one of aluminum is accompanied by the replacement of an atom of sodium by one of calcium is, in my opinion, of special interest, because it offers strong support to the ideas of those who believe that the forces which hold together the atoms in the crystal structures of many substances are comparable with the principal valencies. Indeed, we can think * * * * * that when we replace an atom of silicon by one of aluminum in the structure of albite, the eight oxygen atoms remaining fixed with their sixteen valencies, it necessarily happens, in order that all the valencies of the oxygen may be satisfied, that the atom of sodium must be replaced by one of a bivalent element, such as is calcium.

"The rule of Hiortdahl is, thus, explained. In compounds in which the principal valencies control, the sum of the valencies and the number of the atoms⁶ (or radicals) must remain unchanged in passing from one compound to another by substitution of atoms of different valencies, in order that the crystal form may not suffer great modification."

⁶ "It is necessary also, naturally, that the atoms which replace each other should present certain chemical and structural relations, otherwise the rule will not be followed. The condition that the number of the atoms should remain unchanged was not suggested by Hiortdahl."

In a note to a brief discussion of Langmuir's "Octet Theory of Valence" Zambonini says: "I must again insist on the fact that the particular nature of the atoms that replace each other is of essential importance in order that Hiortdahl's rule may be followed. The isosterism of Langmuir is not applicable: thus, Ca^{++} and Na^+ are not isosteric but, notwithstanding, albite and anorthite are isomorphous; while Na^+ and Mg^{++} are isosteric but a magnesium anorthite does not exist."

Zambonini brings up the isomorphism of diopside, $\text{CaMgSi}_2\text{O}_6$, and acmite, $\text{NaFe}^{+++}\text{Si}_2\text{O}_6$, as an example analogous to that of albite and anorthite, pointing out that iron and magnesium have almost identical atomic diameters, 2.80 and 2.85 Å, respectively, and that the sum of the valencies of CaMg and NaFe^{+++} are equal. He also cites the case of isogonism between triphylite, $\text{LiFe}^{+++}\text{PO}_4$, and olivine, MgMgSiO_4 , which was noted by J. D. Dana in 1854. In this last case the atomic diameters of magnesium and iron are almost the same, as we have seen, and also those of lithium and magnesium (3.0 and 2.85 Å, respectively), while phosphorus is one of the heterologues of silicon. Zambonini finally explains similarly the isomorphism of orthoclase and celsian, the atomic diameters of potassium and barium being, respectively, 4.15 and 4.20 Å, while those of sodium and calcium are 3.55 and 3.40 Å, so that albite and anorthite do not form an isomorphous series with celsian.

It will be seen from the above that Zambonini and Wherry are at one in attributing these cases of isomorphism to the close agreement in atomic diameters or volumes of the "vicariant" elements, but that Zambonini considers as well that equality of the sum of the valencies of the replacing elements is essential, a point which Wherry regards as negligible. In brief, Wherry regards such replacements as simply spatial, or, as he puts it, "connected with volume rather than valence relations," while Zambonini regards them as both spatial and involving the preservation of a balance of forces.

In this connection a statement by Wyckoff⁷ is of interest. Near the conclusion of a paper on the structure of crystals as shown by X-ray study he says: "Such structures as zinc sulphide depart so far from being closely packed arrangements of atoms that some sort of directional character to the forces of combination between

⁷ R. W. G. Wyckoff, *Jour. Franklin Inst.*, **191**, 229, 1921.

their atoms seems necessary to account for their existence as stable groupings." These "directional forces," as appears from the preceding discussion by Wyckoff, are what he terms "valency bondings," so that it would appear that the X-ray study of crystal structure favors Zambonini's view, which implies control by valency, rather than Wherry's simpler, purely spatial one.

It would appear⁸ that Barlow and Pope⁹ were the first, or among the first, as far back as 1906, to suggest that isomorphism depended on the replacement of atoms of similar sizes, as well as on like valency.

STERRY HUNT AND THE THEORY OF THE PLAGIOCLASES

It may be of interest to American mineralogists to add that Zambonini, in another paper,¹⁰ calls attention to the fact that Sterry Hunt¹¹ antedated Tschermak by about ten years in considering the members of the plagioclase group as mixtures of isomorphous albite and anorthite, and that the feldspars intermediate between the extremes are not definite mineral species.

ON STRUCTURE AND ISOMORPHISM IN CRYSTALS

RALPH W. G. WYCKOFF, *Geophysical Laboratory,
Carnegie Institution of Washington*

In a recent number of *THE AMERICAN MINERALOGIST* an interesting paper¹ has appeared which states that "It now seems probable that the principal requisite of isomorphous replaceability is that the elements in question must possess approximately identical volumes, at least in simple compounds, the crystal structures of which represent fairly close packing of the constituent atoms." An abstract² of a paper expressing similar ideas has also been published.

In the second paper^{2,3} it is considered that isomorphous replacement will occur when there is a balancing of the valences of the atoms concerned and when at the same time the volumes of the

⁸ Cf. J. N. Friend, *The Theory of Valency*, 175-181, 1915.

⁹ Barlow and Pope, *Trans. Chem. Soc.*, **89**, 1724, 1906.

¹⁰ F. Zambonini, *Rend. Accad. Lincei*, **31**, 341, (May 7), 1922.

¹¹ T. Sterry Hunt, *Am. J. Sci.*, **18**, 270, 1854; *Phil. Mag.*, **9**, 354, 1855. See also Hunt's *Chemical and Geological Essays*, 444, 1875.

¹ E. T. Wherry, *Am. Mineralogist*, **8**, 1, 1923.

² F. Zambonini [H. S. Washington], *Am. Mineralogist*, **8**, 81, 1923.

³ F. Zambonini, *Rend. Accad. Lincei*, **31**, 295, 1922.

replacing atoms are approximately equal to the volumes of those replaced. In the first article¹ the importance of the valence factor is rather minimized. Unfortunately, from the standpoint of the crystal analyst, the phenomena are not so simple as they thus appear.

To begin with it must be remarked that no general and exact statement of the connection between isomorphism and atomic arrangement can be made at the present time. In most cubic and in all other crystals the positions of atoms will not be fixed solely by symmetry properties. The few experiments yet made show that even in such simple isomorphous crystals as the carbonates of calcium and of manganese, the variable parameters defining the positions of some atoms will not have the same values. Thus it is seen that isomorphous crystals need not, and in general will not, have identical crystal structures. In fact the only field in which identity in the structures of two crystals will be more than an affair of chance is amongst the cubic crystals for which isomorphism itself has lost its usual significance. Because there is no equality between the structures of isomorphous crystals, and because isomorphism has a definite meaning in the field of crystallography itself, it seems more appropriate not to saddle upon it an indefinite crystal-structure import. To meet the need of describing crystals whose structures are sufficiently alike so that they will be crystallographically isomorphous, the term *homeotaxial*⁴ will be employed. Two crystals are to be understood as homeotaxial when they are chemically alike with the same type of atomic arrangement and when the distributions of atoms are so nearly similar that they are isomorphous in the usual sense. Thus pyrite and hauerite are homeotaxial because they are similar chemically, and have the same type of cubic atomic arrangement even though the parameter defining the positions of the sulfur atoms is somewhat different in the two instances; but zinc blende and galena are not homeotaxial, even though they are chemically similar and are both cubic, because the type of atomic arrangement is different in the two. It will be noted that homeotaxial is more specialized in meaning than isomorphous because though all homeotaxial crystals are isomorphous in its widest sense, isomorphous crystals need not have the same sorts of atomic arrangement and consequently may not be homeotaxial. With the existing complete

⁴ The writer wishes to thank H. S. Washington for this term.

lack of knowledge of the atomic groupings in complicated crystals, it is impossible to set any definite limits to the variations of structure within which crystals will remain homeotaxial.

The substitution of an atom for one of a different element in the production of mixed crystals may either leave the mixed crystal homeotaxial with the original or may alter its form markedly. If the replacement is one of the first sort it is an isomorphous atomic replacement.

It would appear that the working basis of the first paper referred to above is contained in the statement that in crystals which are composed of atoms of approximately constant volumes packed closely together, substitution of one atom for another of a different kind without change in the crystallographic characteristics (the axial ratios and angles) can take place whenever the interchanged atoms have practically the same effective volumes.

This view of the nature of crystals is of the greatest antiquity, repeating itself with but slight variations from the time of the ancient philosophers to the present. Some 25 years ago it was developed at considerable length by Sollas,⁵ who, however, did not look upon crystals as necessarily close-packed structures. Barlow and Pope⁶ in adding their assumption correlating valency with volume made these atomic spheres close-packed. In its latest appearance as the hypothesis of constant atomic radii W. L. Bragg⁷ stresses the constancy of the radius (and volume) of an atom from crystal to crystal. The information from crystal structure study using X-rays offers the chance of testing out these views. It must be said that the existing data do not accord with either close-packing or constant size⁸ of atoms. In crystals that are homeotaxial there is an additivity of atomic dimensions which may, if desired, be expressed in terms of an hypothesis of constant atomic radii. Between other crystals not homeotaxial this additivity no longer holds, the variation from it apparently becoming greater the less alike are the structures of the crystals involved. Hence the atomic radii calculated from the various crystals which can serve as starting points may be quite different from one another. If the radius of the cadmium atom is calculated from metallic cadmium,

⁵ W. J. Sollas, *Proc. Roy. Soc. London*, **68**, 270, 1898, etc.

⁶ Barlow and Pope, *Trans. Chem. Soc.*, **89**, 1724, 1906.

⁷ W. L. Bragg, *Phil. Mag.*, (6) **40**, 169, 1920.

⁸ R. W. G. Wyckoff, *Proc. Nat. Acad. Sci.*, **9**, 33, 1923.

the radius of oxygen obtained from this value for cadmium through cadmium oxide, and the size of other atoms reached by the simple extension of this process to other crystals, the resulting series of atomic dimensions would be somewhat different from those derived from the related metallic zinc, for instance. They would also differ from those deduced from the diamond as a starting point or from the series calculated through pyrite. In fact the results of all of these series that have been mentioned would be unlike. It is seen thereby that the hypothesis of truly constant atomic radii is experimentally disproved. Still the "radius" of a particular atom may not be expected to be enormously greater, meaning thereby several times greater by volume, in one crystal than in another. The point of importance to this discussion, however, lies in the fact that except possibly in some of the strongly electropositive and electronegative atoms the difference in size between various atoms may not be greater than the changes in dimensions of the same atom in passing from one sort of a crystal to another. By choosing for discussion examples of replacement which involve the alkali and alkaline earth metals, the most favorable cases have been considered, but the myriad of replacements which should be possible but are not found amongst the rest of the atoms in crystals under the explanation now being discussed have been ignored.

While this idea of constant atomic radii may perhaps be thought of as holding somewhat approximately, in the sense that the radius of one kind of atom probably does not change by multiples of its own size, the other part of the view, which regards crystals as closely packed structures, runs absolutely counter to the results of crystal analysis. Aside from the simple metals, the large majority of structures which have thus far been elucidated are more or less distended arrangements of atoms. Furthermore at the present time there is no information which might lead us to understand either why the atoms within a crystal do not closely pack together, or why, for compounds which seem closely related to one another, some will have one kind of an arrangement while others may be possessed of a totally different one. Examples of these differences in structure could be multiplied almost without limit. Thus the sodium chloride arrangement, which is itself not a very close-packed grouping of spheres, is a common one for the alkali halides and the oxides, sulfides, etc. of divalent metals. Yet its failure to be a universal one is clear from Table 1.

TABLE 1

| NaCl grouping | | NH ₄ Cl grouping | Cubic ZnS grouping | ZnO grouping |
|---------------|-------------------|-----------------------------|--------------------|--------------|
| LiX | NaX | CsCl | CuCl | AgI |
| KX | RbX | CsBr | CuBr | CdS |
| CsF | NH ₄ I | CsI | CuI | ZnS |
| MgO | CaO | TlCl | ZnS | ZnO |
| CdO | AgCl | NH ₄ Cl | | |
| NiO | AgBr | NH ₄ Br | | |
| CaS | MnS | | | |

NOTE: In this table X will represent any of the halogen atoms.

In the face of the overwhelming crystal structure evidence it is impossible either to make the assumption that crystals are closely packed or at the present time to prophesy anything about atomic arrangement in advance of experimental determinations.

Many data are at hand to show that neither homeotaxis nor isomorphism is determined primarily by the effective "sizes" of atoms. For example among the simple compounds, similar crystals of such widely different molecular volumes as lithium fluoride and caesium fluoride are completely homeotaxial, as are the more complicated potash and caesium alums; and iodine can be substituted for chlorine in the hexammonates of the nickel halides, for instance, without any alteration of atomic arrangement.

The possibility of solid solution between albite and anorthite is accounted for in the papers^{1,2,3} under consideration by saying that the sum of the "volumes" of the replacing calcium and aluminum of the one crystal is equal to the sum of the replaced sodium and silicon of the other. If this criterion were the basic one it should be possible to effect a replacement of this sort in the cubic garnets, calcium and aluminum being replaced by sodium and more silicon. This should be true under the conclusions laid down in both of these papers, for not only would no change in volume take place but also there is a complete balancing of valences. As a matter of fact no cubic mixed garnets of this sort are found.

There probably can be no quarrel with the statement that isomorphous atomic replacements, or solid solution formation, will not take place unless the interatomic distances of the corresponding atoms involved in the substitutions are closely similar. This fact,

which has long been known in the form of the rule of equal molecular volumes and is often emphasized, can of course be expressed in terms of "atomic radii," taking due recognition of the indefiniteness of these "atomic dimensions." The results of crystal analysis do not, however, justify that extension of this idea which finds in this equality of interatomic distances the primary cause and principal determining factor of isomorphous atomic replacements. In the absence of any real knowledge of the atomic arrangement in crystals with low symmetry, the precise nature of the other governing factors remains unknown as heretofore and no satisfactory explanation of such complex solid solutions as arise from albite and anorthite can be offered.

Nevertheless a somewhat more detailed discussion of the requirements of these mixed feldspars may throw some light upon the general character of other factors. In crystals of high symmetry experiment has shown that most, if not all, of the atoms of a given chemical kind have atoms of other sorts distributed about them in identically the same manner, that is they are *equivalent* to one another. In arrangements of less and less symmetry it is generally true that fewer and fewer of the chemically like atoms are equivalent. Thus, whatever the structure of the calcium aluminum garnet $[\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}]$ may be, it is quite certain that either all of the atoms of a sort are equivalent or that they fall into a few groups of equivalent atoms. In anorthite $[\text{CaAl}_2\text{Si}_2\text{O}_8]$ the low degree of symmetry precludes the possibility of an equivalence of many of its atoms. This non-equivalence of the atoms in crystals of low symmetry, combined with the fact that most of them have positions not completely fixed by symmetry requirements, presents the possibility of building up many arrangements which are nearly but not exactly alike both in atomic grouping and in dimensions of the unit cells. It would appear that albite and anorthite are two such similar structures. How closely the positions of the sodium and silicon atoms of the one approach to the positions of the calcium and aluminum atoms of the other it is now impossible to say.

In the simple isomorphous replacement of but one kind of atom in a crystal, for instance in the formation of mixed crystals of KCl and KBr, the replacing bromine atoms, let us say, apparently can occupy any chlorine positions within the crystal and will be distributed in a haphazard fashion. A simple isomorphous mixing

of barium in anorthite would not be expected for the same reason that sodium and rubidium chlorides do not mix, that is, because the unit cells probably differ too much in size, or because their molecular volumes are too unlike, or because the atomic "radius" of rubidium or of barium is too much greater than that of sodium or of calcium. Any of these "explanations" may be used for they all express the same idea. In such dual replacements as occur when albite and anorthite mix, where the replacing and replaced atoms are not chemically similar, the distribution must be more complex than in simple replacements. For if the inserted pair are not intimately associated together in place of those removed, the requirements of (electrical) stability of the structure will be disturbed in that small region. It consequently would seem necessary that these mixed feldspars should be constituted somewhat as if they were composed of an intimate mixing of albite and anorthite groupings of atoms. Geometrically it might be pictured much as if one unit cell had the albite arrangement while neighboring ones might be possessed of that of anorthite. Of course it must be borne in mind that this is only a diagrammatic representation, for in a real crystal some of the atoms of one unit cell will always be shared by those of neighboring cells. At the same time it may well be that the distribution in one part of a unit is that of albite and in the rest that of anorthite. The essential difference between this kind of a replacement and the simple one in which the entering atoms can go into the structure one by one and in any position requires emphasis.

The influence of the symmetry upon the ease with which such dual replacements can take place is clearly shown by a contrasting of anorthite with the calcium aluminum garnet. From the former it is only necessary to pass to the other end member (albite) of a conceivably isomorphous series by the substitution of a single group of sodium and silicon atoms for the calcium and aluminum. Because of the large equivalence of chemically like atoms in the cubic garnet several pairs of atoms would have to be interchanged simultaneously in order to obtain a possible end member of such a series. Even then it might happen that in many instances no such end member would be geometrically, not to mention physically, possible. Though the structure of the garnet is not sufficiently well known to permit of a definite statement, it is probable that such a cubic sodium silicon garnet could not exist.

Enough has been said to show that too few data are at hand to give an adequate explanation of isomorphous mixing, even in the relatively simple example of albite and anorthite.

The writer wishes to express his gratitude to H. E. Merwin and to H. S. Washington for discussions of this subject.

RECENTLY DESCRIBED "BISBEEITE" FROM THE GRAND CANYON IS CYANOTRICHITE

SAMUEL G. GORDON, *Academy of Natural Sciences of Philadelphia*

In a recent paper in this journal¹ entitled "The Optical Properties and Morphology of Bisbeeite," Professor Austin F. Rogers described a blue mineral, occurring as minute fibrous spherulites in the Grandview mine, Grand Canyon, Arizona. His identification of the material as representing this species was based on the agreement of his optical data with that for bisbeeite, as determined by W. T. Schaller and recorded in Dana, Appendix 3, p. 14; however, Dr. Schaller informs the writer that the value of 1.65 there given for γ represents an intermediate value between β and γ . Although E. S. Larsen² definitely states that he used the original material for a more precise determination of the properties given, Rogers considers it "doubtful whether he worked with the original material." Dr. Larsen informs the writer that not only is his published statement correct, but that he has recently redetermined the values, completely confirming his previous data.

Two very beautiful specimens of this mineral, consisting of methyl-blue capillary crystals, are in the collection of Mr. George Vaux, Jr., Bryn Mawr, Pa., and these were identified optically by the writer as the orthorhombic copper aluminum sulfate, cyanotrichite. They give a copious reaction for sulfur by the usual tests. A comparison of Rogers' data with that of cyanotrichite indicates his material to be that mineral, and not bisbeeite, as may be seen by inspection of the accompanying table.

This conclusion is further substantiated by Rogers' statement: "Although a silicate, it is noteworthy that fragments of the mineral are soluble in a molten sodium metaphosphate bead." As the mineral is a sulfate and not a silicate, this chemical behavior is to be expected.

¹ *Am. Min.*, 7, 153-154, 1922.

² Microscopic Determination of Non-opaque Minerals, *U. S. Geol. Survey, Bull.* 679, p. 48.

OPTICAL PROPERTIES OF CYANOTRICHITE AND BISBEEITE

| | Cyanotrichite, ¹ Tintic, Utah (Larsen) | Grand Canyon ² mineral (Rogers) | Bisbeeite ³ (original material Larsen) |
|--------------|---|--|---|
| Color | Bright blue | Methyl blue | Nearly white |
| Form | Needles | Fibrous spheru- lites | Cotton-like |
| Orientation | $Z=c$ | $Z=c$ | $Z \parallel$ elongation |
| Sign | + | + | + |
| Pleochroism: | | | |
| X | Colorless | Neutral | Nearly colorless |
| Y | Pale blue | Pale bluish-green | Nearly colorless |
| Z | Bright blue | Deep blue | Pale greenish |
| Indices: | | | |
| α | $1.588 \pm .003$ | $1.589 \pm .001$ | $1.615 \pm .01$ |
| β | $1.617 \pm .003$ | $1.620 \pm .001$ | $1.625 \pm .01$ |
| γ | $1.655 \pm .003$ | $1.649 \pm .001$ | $1.71 \pm .01$ |

¹ Larsen: *U. S. G. S. Bull.*, **679**, 65, 1921.

² Rogers: *Am. Min.*, **7**, 153, 1922.

³ Larsen: *U. S. G. S. Bull.*, **679**, 48, 1922.

PROCEEDINGS OF SOCIETIES

THE MINERALOGICAL SOCIETY OF WASHINGTON, D. C.

For a number of years there has existed in Washington an informal organization known as the Petrologists' Club, before which numerous papers on petrology and allied sciences have been presented and critically discussed, to the advantage of all concerned. Early in 1923 several mineralogists talked over the desirability of organizing a similar society at which papers of more directly mineralogical nature might be similarly presented and informally discussed. W. F. Foshag agreed to act as Secretary, and sent out a number of invitations for a meeting at the residence of W. T. Schaller, 1637 R. St. N. W., on the evening of Friday, February 23rd, 1923. Braving the coldest weather of the winter, the following 13 mineralogists were present, thus expressing their approval of the formation of this society: W. S. Burbank, W. F. Foshag, H. Insley, E. S. Larsen, H. E. Merwin, C. S. Ross, E. B. Sampson, W. T. Schaller, F. C. Schrader, G. Steiger, E. T. Wherry, R. W. G. Wyckoff, and T. D. Shipton of Hanover, Ill., a member of the Mineralogical Society of America, visiting in Washington.

The first paper presented was by W. T. Schaller: **Ptilolite and related zeolites**. Several of these high-silica, acid-insoluble zeolites have been described, but conflicting statements as to their relationships appear in the literature. Recently Bøggild has urged the identity of "flokite" with ptilolite, and T. L. Walker the identity of ptilolite with mordenite. By correlating published data as to composition, crystallography, and optical properties, supplemented by new determinations (by Schaller, Ross, and Shannon), it is clearly shown that three distinct species are represented:

1. Mordenite (How, 1864), containing 9 SiO_2 and $6\text{H}_2\text{O}$ for 1 Al_2O_3 and 1 $(\text{Ca}, \text{Na}_2)\text{O}$. Monoclinic or triclinic with inclined extinction (about 5°). Includes "flokite" (Callisen, 1917), which was determined by its author to have this extinction angle and composition, whereas Bøggild's specimens with orthorhombic crystals must have been the next mineral.

2. Ptilolite (Cross and Eakins, 1886), with 10 SiO_2 and $7\text{H}_2\text{O}$. Orthorhombic, with parallel extinction. This is the commonest species.

3. Another mineral, described by Pirsson from Wyoming in 1890, and accepted by Dana as crystallized mordenite, but evidently a dimorphous form of ptilolite since it has 10 SiO_2 and $7\text{H}_2\text{O}$. It is monoclinic and agrees with heulandite in crystallization, has a large extinction angle, and the habit is not fibrous but tabular. It is proposed to rename this mineral from Wyoming, **Clinoptilolite**, referring to its *inclined* extinction but agreement in composition with *ptilolite*.

It seems evident that the only way for progress to be made in the interpretation of such groups of minerals is to obtain complete data for individual occurrences, and not use the composition of one, the crystallization of a second and perhaps the optical properties of a third, as is often done.

The second paper was by E. T. Wherry: **Volume isomorphism in minerals**. As it is not proposed to publish this separately, it is here abstracted in detail. Two published articles on silicates (*This journal* 7, 113 and 8, 1) were reviewed, and a general theory of the relations proposed, this being illustrated by the sesquisulfide minerals as follows:

ISOMORPHOUS GROUPS OF ELEMENTS

| | | | | | | | | |
|----|----|----|---|--------------------|----|--------------------|----|---|
| As | 9 | S | 6 | (OS_2) | 13 | (STe_2) | 24 | The numbers represent atomic vol- |
| Sb | 12 | Se | 7 | (S_3) | 18 | (Se_3) | 21 | umes, in 10^{-24} cc. units, based on X-ray |
| Bi | 13 | Te | 9 | (SSe_2) | 20 | (Te_3) | 27 | data, but are admittedly only rough |
| | | | | | | | | approximations. |

MINERALS OF THE SESQUISULFIDE DIVISION

| Orpiment Group | Stibnite Group | Tetradymite Group |
|--|--|--|
| Monoclinic; β near 90° . | Orthorhombic | Rhombohedral |
| $a:b:c$ near $0.6:1:0.8$. | $a:b:c$ near $1:1:1$. | $a:c$ near $1:1.6$. |
| Orpiment..... $\text{As}_2 \text{S}_3$ | Stibnite..... $\text{Sb}_2 \text{S}_3$ | Tetradymite... $\text{Bi}_2 \text{STe}_2$ |
| Kermesite..... $\text{Sb}_2 \text{OS}_2$ | Bismuthinite... $\text{Bi}_2 \text{S}_3$ | Platynite (?)... $\text{Bi}_2 \text{Se}_3$ |
| | Guanajuatite... $\text{Bi}_2 \text{SSe}_2$ | Tellurobismu- |
| | Selenobismu- | thite..... $\text{Bi}_2 \text{Te}_3$ |
| | thite..... $\text{Bi}_2 \text{Se}_3$ | |

The theory suggested is that in such a series of compounds some intermediate set of elements yields the most stable arrangement, and that entrance of either larger or smaller atoms may distort this arrangement and result in change of symmetry. Taking stibnite, the best crystallized member, as the typical one, replacement of either of its kinds of atoms by smaller ones leads at once to decrease in symmetry (orpiment group); while replacement by larger ones at first causes no change except diminution of ability to form good crystals (stibnite group) but ultimately results in increased symmetry (tetradymite group).

When a very simple crystal structure is represented (*e. g.*, that of NaCl , PbS , etc.) such relations may not hold because the structure can remain stable during marked changes in sizes of the atoms. On the other hand when the structure is

highly complex, the distortion due to the entrance of larger or smaller atoms can be so distributed among numerous other atoms as not to affect the crystallization ("mass-isomorphism"). It is believed, however, that the volume relations here outlined do exist in a considerable number of cases where the structure is of intermediate complexity.

By way of discussion H. E. Merwin read an abstract, prepared by H. S. Washington (who was unable to be present owing to absence from the city) of two papers by Professor F. Zambonini of Italy, showing that he had reached essentially the same conclusions as Wherry with respect to the relations between Na, Ca, K and Ba in the feldspars, although emphasizing in addition the valence relations. (See page 81 of this issue.)

R. W. G. Wyckoff then presented his view that the relations pointed out as existing in the silicates and sulfides were little more than matters of chance, and that the whole idea of volume isomorphism is hardly in accord with the results of the more dependable X-ray data. (See page 85 of this issue.) These show that crystals are in general not close-packed structures, so that slight changes in volumes of the constituents should not yield marked effects; that the Bragg view of constancy of atomic volume is untenable, some atoms changing a hundred per cent or more on passing from one mode of combination to another [*e.g.* nickel in the hexamminates of its halides (*J. Am. Chem. Soc.*, **44**, 1239, 1922) occupies a much greater volume than it does in the metallic state]; and finally that many of the published estimates of atomic dimensions from X-ray measurements are erroneous in that the workers have incorrectly interpreted the experimental data.

In reply the speaker stated that close-packing in the strict sense was unnecessary to the theory; that even though elements do vary from one compound to another it seemed probable that the variation would be similar for all the elements in small isomorphous series, so that their relative positions in the series would be unchanged; and that while admittedly the absolute magnitudes in the literature are often inexact, the atomic volumes of enough elements are definitely known to indicate the general trend of the relationships presented.

After two hours spent on this scientific program, the members adjourned for refreshments. The steering committee (composed of W. F. Foshag, Secretary, W. T. Schaller and E. T. Wherry) proposes that the next meeting shall consist of a field trip to the diabase quarry at Goose Creek, Va., where zeolites and their associated minerals are being obtained in interesting paragenetic relations; also Earl V. Shannon, who is working up the material, desires considerable rock material brought to Washington.

EDGAR T. WHERRY, *Secretary pro tem.*

PHILADELPHIA MINERALOGICAL SOCIETY

Academy of Natural Sciences of Philadelphia, March 8, 1923

A stated meeting of the Philadelphia Mineralogical Society was held on the above date with the president, Mr. Vaux, in the chair. Nineteen members and four visitors were present.

Mr. Frederick Oldach addressed the society on "THE PEGMATITES." The physical characters, mineralogy, origin, and classification of the pegmatites were discussed, with descriptions of typical pegmatite deposits. Mr. Hoadley made some supplementary remarks regarding the pegmatites of Connecticut.

The following were proposed for active membership: Messrs. Andrew Mantz and Frank K. Pickel.

Mr. Biernbaum reported a trip taken with Mr. Hallowell, to Moore, Delaware County, where they found cyanite. Mr. Blank exhibited sillimanite from the Wissahickon.

SAMUEL G. GORDON, *Secretary*.

BOOK REVIEW

MINÉRALOGIE DE MADAGASCAR. A. LACROIX. *Paris*. A. Challamel. Vol. I, xvi+624 pages, 27 plates, 1 map in colors, and 504 figures. Vol. II, vii+694 pages, 29 plates, and 11 figures. 1922.

The first part of this two volume work (pp. 1-148, vol. I) is a description of the GEOLOGY AND GEOGRAPHY of Madagascar.

In part 2, MINERALOGY (pp. 149-604, vol. I), the individual minerals (195 in number) found on the island are discussed in systematic order. A general description of each mineral is followed by detailed particulars of its occurrences in Madagascar, with analyses and optical determinations, in a manner quite similar to that adopted by the author in his "MINÉRALOGIE DE LA FRANCE ET DE SES COLONIES." This section is illustrated by 27 excellent plates of photographs, and 504 crystal drawings. A large map of the island is found at the end of volume one.

ECONOMIC MINERALOGY is discussed in part 3 (pp. 1-218, vol. II). Here are described: deposits of precious metals, common metals, gems and ornamental stones, rare metals (including radioactive minerals), mica, graphite and corundum, salt, etc., building stones, coal and petroleum. Next the writer treats of the mineral springs. Statistics of mineral production conclude this part. Part 3 contains 23 plates illustrative of mineral deposits and mining methods, as well as a number of sketch maps.

The fourth part of this work is entitled LITHOLOGY (pp. 219-665, vol. II). It includes descriptions of the intrusives of the crystalline massif, the schistose rocks, and post-Lias intrusives. Many analyses are given, and a number of plates illustrating thin sections of rocks. The detailed treatment of pegmatities, in which those of Madagascar are compared with other pegmatites the world over, may be especially mentioned.

This is in every way an excellent work. It is perhaps not too much to say that it can be regarded as a classic in the field of books on regional mineralogy.

E. F. H.

ABSTRACTS: CRYSTALLOGRAPHY

THE CRYSTALLOGRAPHY OF SOME HEAVY METAL ACIDS AND SALTS OF PYROCATECHIN. P. J. BEGER. *Centr. Mineral.*, 129-42, 1920.

This paper gives the crystallography and optical properties of the following: tri-pyrocatechin arsenic acid, its Cr, Co, and Ni salts; the Na salt of dipyrocatechin nickel acid, and the NH_4 salt of pyrocatechin molybdenum acid.

E. F. H.

CRYSTALLOGRAPHIC PROPERTIES OF SULFONAL. H. SEIFERT. *Centr. Mineral.*, 97-101, 1920.

Sulfonal, $\text{C}_7\text{H}_{16}\text{S}_2\text{O}_4$ is monoclinic holohedral, $a:b:c = 1.563:1:1.446$, $\beta = 90^\circ 31'$. The habit is varied and dependent upon the solvent from which the substance is crystallized.

E. F. H.

REGULAR GROWTHS OF CRYSTALS AND TWINNED INTER-GROWTHS. GEORG KALB. *Centr. Mineral.*, 285-8, 1920. REGULAR GROWTHS OF CRYSTALS AND CRYSTAL STRUCTURE. GEORG KALB, *ibid.*, 321-3, 1920.

The first is largely a critical discussion of Johnsen's paper on twins (*Neues Jahrb. Mineral.*, Beil.-Bd. 23, 237-344, 1907). In the second paper, from a review of Schmidt's study of parallel fibrous halite and gypsum (*Diss. Halle*, 1911) K. concludes that the crystals arrange themselves in oriented position on their support.

E. F. H.

FURTHER LAUE METHODS. R. GROSS. *Centr. Mineral.*, 52-64, 1920.

This paper describes an instrument for the measurement of Laue photographs, an apparatus for the Roentgenometric detn. of very small, crystallographically unorientable objects, and a method for the systematic investigation of the symmetry elements.

E. F. H.

THE CRYSTAL STRUCTURES OF WULFENITE AND SCHEELITE. ROSCOE G. DICKINSON. *J. Amer. Chem. Soc.*, 42, 85-93, 1920.

Studies of X-ray spectra from several crystal planes show that wulfenite and scheelite have probably a face-centered lattice, with the atoms so located as to form a "diamond" arrangement.

E. F. H.

THE CRYSTALLOGRAPHY OF MELEZITOSE. EDGAR T. WHERRY. *J. Amer. Chem. Soc.*, 42, 125-8, 1920.

Melezitose dihydrate ($C_{18}H_{32}O_{16} \cdot 2H_2O$) is orthorhombic, $a:b:c = 1.216:1.0496$, forms a, b, d, e, m ; $\alpha = 1.540$, $\beta = 1.548$, $\gamma = 1.550$ (for Na); ext. parallel; $2E = 85^\circ$; opt. -; $X = a$, $Y = b$, $Z = c$.

E. F. H.

METHYL AND ETHYL AMMONIUM MERCURIC IODIDES: THEIR PREPARATION, CRYSTALLOGRAPHY, AND OPTICAL PROPERTIES. GEORGE S. JAMIESON AND EDGAR T. WHERRY. *J. Amer. Chem. Soc.*, 42, 136-45, 1920.

The crystallography and optical properties are given for: $(CH_3)_2NH.HI.HgI_2$ (monoclinic); $(C_2H_5)_2NH.HI.HgI_2$ (orthorhombic); $(CH_3)_3N.HI.HgI_2$ (orth.); $(C_2H_5)_3N.HI.HgI_2$ (mono.); $(CH_3)_4NI.HgI_2$ (orth.); and $(C_2H_5)_4NI.HgI_2$ (tetragonal).

E. F. H.

THE CRYSTAL STRUCTURE OF CAESIUM DICHLORO-IODIDE. RALPH W. G. WYCKOFF. *J. Amer. Chem. Soc.*, 42, 1100-16, 1920.

The body-centered unit rhombohedron contains one molecule of $CsCl_2I$. The disposition of the several atoms is given.

E. F. H.

RELATIONSHIPS BETWEEN GROWTH FORMS AND STRUCTURE OF CRYSTALS. PAUL NIGGLI. *Z. anorg. allgem. Chem.*, 110, 55-80, 1920; through *Chem. Abstr.*, 14, 3354, 1920.

The faces which attain maximum development in the growth of xls. correspond with the principal planes in the lattice structure. Faces with complex indices grow more swiftly than simpler faces. Calculations on a number of cubic xls. show that the theoretically most probable faces are those which do actually occur.

E. F. H.

THE MOLECULAR DIRECTING FORCE OF LIQUID CRYSTALS. O. LEHMANN. *Z. anorg. allgem. Chem.*, **113**, 253-300, 1920; through *Chem. Abstr.*, **15**, 2763, 1921.

The properties of liquid xls. are best accounted for on the assumption that they have a leaflet-like structure, the units of which endeavor, as far as possible, to lie parallel, but which can glide freely in a direction parallel to their faces. E. F. H.

THE CHEMISTRY AND CRYSTALLOGRAPHY OF SOME FLUORIDES OF COBALT, NICKEL, MANGANESE AND COPPER. FLOYD H. EDMISTER AND HERMON C. COOPER. *J. Amer. Chem. Soc.*, **42**, 2419-34, 1920.

The acid fluorides of Co, Ni, and Mn, formula $\text{RF}_2 \cdot 5\text{HF} \cdot 6\text{H}_2\text{O}$, give rhombohedral crystals, with prismatic cleavage; opt. +. The Cu salt is probably monoclinic. E. F. H.

THE EFFECT OF ASYMMETRY: A STUDY IN CRYSTAL STRUCTURE. THOMAS V. BARKER AND MARY W. PORTER. *J. Chem. Soc., (Trans.)* **117**, 1303-21, 1920.

This investigation shows that racemic crystals of phenylbenzylmethylethylammonium mercuri-iodide are isomorphous with the corresponding diethyl derivative, although the racemic crystals contain two kinds of asymmetric molecules, while in the diethyl derivative all the molecules are identically similar and symmetrical. Crystallographic measurements and figures for nineteen compounds of alkylammonium, phenylalkylammonium and phenylbenzylalkylammonium are given.

E. F. H.

MINERALOGY

MELTING AND TRANSFORMATION PHENOMENA OF SPODUMENE. F. MEISSNER. *Z. anorg. allgem. Chem.*, **110**, 187-95, 1920.

Natural (α) spodumene is slowly transformed into β -spodumene at temps. as low as 690° . With increasing velocity in rise of temp. the transformation temp. is raised. At ordinary pressures the transformation appears to be irreversible.

E. F. H.

THE ARRANGEMENT OF THE ATOMS AND OPTICAL ROTATION IN QUARTZ AND SODIUM CHLORATE. J. BECKENKAMP. *Z. anorg. allgem. Chem.*, **110**, 290-310, 1920; through *Chem. Abstr.*, **14**, 3354, 1920.

A structure in which the Si atoms form a rhombohedral lattice is proposed for quartz. The spiral structure appears with the introduction of the O atoms. Their disposition is such that the orientation of valency directions is the same in horizontal or vertical molecular layers. This accounts for the optical rotation. The total structure is made up of nine 3-sided, prismatic lattices. The different kinds of twin xls. of quartz, and the relation of quartz to tridymite, β -quartz, and cristobalite are discussed. NaClO_3 has a structure similar to that of calcite, the Ca atoms being replaced by those of Na, C by Cl.

E. F. H.

SULFUR IN COAL, GEOLOGICAL ASPECTS. GEO. H. ASHLEY. *Trans. Am. Inst. Mining Eng.*, **63**, 732-8, 1920.

A presentation of the various modes of occurrence of sulfur in coal.

A. S. WILKERSON.